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16. ABSTRACT

A sulfuric acid review conference sponsored by EPA's automotive Catalyst Research Program was held recently at Hendersonville, NC, for researchers whose work is funded by EPA. Emissions characterization research indicated that in-use catalyst-equipped vehicles emit low levels of H_2SO_4, averaging 2.7 mg/mile for 49-state cars and 15 mg/mile for California cars. Research on measurement methodology for H_2SO_4 and other sulfate compounds has led to the development of several promising techniques based on selective volatilization. In-roadway and off-roadway monitoring programs are providing sulfate data which can lead to improved mathematical predictive models. Acute toxicity studies to date indicate that morphological, biochemical, physiological, and pharmacological alterations due to inhaled H_2SO_4 alone do not appear to occur at levels less than 1 mg/m^3. However, striking effects are noted with combinations of H_2SO_4 and other pollutants. Participants identified the need for long term chronic H_2SO_4 exposure studies.

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Characterization and Measurement Methodology Development

Current Status

Research on characterization and measurement includes the chemical identification and quantification of sulfate and other pollutants; the development of chemical and instrumental methods for the analysis of sulfuric acid and other sulfate compounds; and the development of mobile in-roadway sampling methods and strategies.

Although both monolith and pelleted catalysts can emit H_2SO_4 in varying amounts, recent EPA emissions testing research has shown that pelleted catalysts—which typically consist of Al_2O_3 and noble metals—will store H_2SO_4, probably by surface adsorption, resulting in desorption of SO_2 and emission of lesser amounts of H_2SO_4 at higher temperatures. This occurs when the exhaust gas is reducing in character in the presence of hydrocarbons or CO. These and other studies indicate that the emission of sulfur compounds is related to the condition and type of catalyst used, sulfur content of gasoline, age of the catalyst, and driving conditions. The dynamometer sulfate emissions test cycle (S-7) was developed with computer simulations by EPA and is now the cycle in general use for determining sulfuric acid emissions. EPA's emissions testing research has also resulted in a method for measuring soluble sulfate in auto exhaust based on the formation of chloranilic acid from barium chloranilate.[7]

Two large scale emissions testing programs for in-use vehicle fleets are in process by EPA contractors. Olson Laboratories is testing 101 consumer owned California 1975 and 1976 automobiles after approximately 3500, 7500, and 12,500 miles.[8] Using the S-7 cycle, Olson Laboratories found that sulfate emissions were low, averaging 15 mg/mi for the fleet. As the odometer readings increased, emissions of CO and hydrocarbons increased but sulfate emissions decreased. The New York State Department of Environmental Conservation is testing 49 consumer owned 1975 and 1976 catalyst-equipped automobiles designed to meet the 49-State or Federal standards.[9] Using the S-7 cycle, tests have been carried out at 5000 mi intervals. As in the Olson Laboratories study, sulfate emissions were low, averaging 2.7 mg/mi for 27 tests, considerably lower than California vehicles. High idle CO, activation of the catalyst, low fuel sulfur levels, and the absence of an air pump combined to yield low sulfate values in most instances.

The Cabot Corporation has developed an instrument for determining ambient levels of sulfuric acid.[10] Sulfuric acid is collected on a non-reactive Teflon filter followed by selective volatilization into a flame photometric detector using hot dry air. At a volatilization temperature of 180°C, interferences from $(NH_4)_2SO_4$ and $(NH_4)HSO_4$ were observed; volatilization at 150°C reduced the effects from these interferences. Specific methods for determining H_2SO_4 in air are under development by Southern Research Institute and include thermal volatilization coupled with sulfur-specific flame photometric detection, and benzaldehyde extraction combined with barium thorin microtitration. Atlantic Research Corporation is identifying reagents which will chemically stabilize H_2SO_4 to form sulfur-bearing adducts that can be analyzed in the presence of otherwise interfering sulfates. Volatile amine compounds are under study which could react rapidly with H_2SO_4 to form amine sulfate and bisulfate salts. The possible use of chemical ionization mass spectrometry to distinguish between H_2SO_4 and $(NH_4)_2SO_4$ at 55°C was described by Pennsylvania State University.

EPA presented an overview of methods used to characterize sulfur in ambient aerosols. Although no single method is completely satisfactory at the present, a number of techniques are being developed and evaluated including aerosol size fractionation with a dichotomous sampler[11] followed by x-ray fluorescence (XRF) analysis; use of selective reactions to produce secondary products that induce chemiluminescence (Geomet Corporation); chemical species identification using Grans titration for H^+; and XRF, thorin colorimetry, and flash pyrolysis for sulfate and sulfur analysis. A method for the determination of total sulfur in gasoline by gas chromatography with a flame photometric detector was also presented by EPA.[12]

The University of Minnesota is engaged in three areas of research to develop methods for sulfuric acid and other sulfur compounds in air. An electronically modulated flame photometric detection system has a minimal response to interferences and can detect levels of sulfur from 0.3 to 0.5 $\mu g/m^3$. A thermal speciation technique permits determination of H_2SO_4 at 71°C, $(NH_4)_2SO_4$ and $(NH_4)HSO_4$ at 142°C, and other refractory sulfates at 190°C. A trichotomous sampler is under development for separating particles into three size fractions: >3.5 μm, 3.5 to 0.08 μm, and <0.08 μm diameter. The sampler is basically a combination of a dichotomous sampler[11] with an electrical aerosol analyzer modified to function as an electrical classifier with a cut size of 0.08 μm diameter. The University of Minnesota is also studying means of generating ultrafine particles of H_2SO_4 for use in inhalation toxicology studies. Using a syringe pump nebulizer system, particles of 0.02 to 0.2 μm diameter by volume have been generated.

Development of field methods for measuring H_2SO_4 and other sulfates on roadways to determine the exposure of vehicle occupants in the Los Angeles area is under way at Rockwell International, Cal Tech, EPA, and the University of Minnesota.[13] An October 1976 field program in Los Angeles used three mobile laboratories to make measurements in the roadway and at nearby background sites. The sulfate concentrations in the roadway attributed to catalyst-equipped vehicles were small enough in comparison with the background sulfate concentrations that they were obscured by data scatter on most days. However, on two days during the October sampling period, the mean value of the roadway sulfate detected above background was 0.6 $\mu g/m^3$. These results led the investigators to conclude that sulfate emissions from catalyst-equipped vehicles are a small part of the total aerosol emissions from roadways at this time. These studies may lead to the development of sampling strategies for estimating the exposure of vehicle occupants to H_2SO_4.

Research Recommendations

There is a continuing need for in-roadway data measurements in order to assess the ever changing emissions composite exhibited by in-use vehicles. Studies should determine what forms of sulfur compounds may be emitted from catalyst systems under various engine conditions. Inhalation exposure studies should simulate as closely as possible the gaseous and aerosol mixtures found on the roadway. It is recognized, however, from theoretical considerations that ultrafine H_2SO_4 particles cannot exist at levels greater than 100 $\mu g/m^3$ in an exposure chamber without coagulating to larger particles. Research should also determine the time scale for the neutralization of H_2SO_4 in ambient air, especially in the nuclei and the accumulation particle modes.

Monitoring

Current Status

Two major monitoring projects are conducted under the *Catalyst Research Program:* the Los Angeles Catalyst Study (LACS)[14] at the San Diego Freeway and the Research on Automobile Pollutant Dispersion Study (ROADS) on the Long Island Expressway. The main objective of the LACS experiment is to obtain ambient air sulfate and other

emission pollutant data both before and after introduction of the 1975 model year catalyst automobiles. The study was started in the spring of 1974 and is the longest term, fixed site highway monitoring effort to date. In addition to providing data on long term sulfate trends and data for possible use in developing models, the LACS site has been valuable for field testing and evaluating newly developed air monitoring instruments such as the massive volume air sampler which can size fractionate and collect gram quantities of suspended particulate matter.[15] Particulate and gaseous pollutants are measured upwind and downwind from the highway with a broad range of sampling devices including hi-vols, membrane filter samplers, cascade impactors, dichotomous samplers, and continuous analyzers for CO, NO, NO_2, O_3, and total sulfur. Other associated measurements made include traffic speed and count by lane, ambient temperature and dewpoint, wind speed and direction, and sulfur and lead content of gasoline used in the area. Although the large volume of data collected is still being analyzed and will be reported shortly at another conference,[16] roadway produced sulfate as measured by the hi-vol averaged about 3 $\mu g/m^3$ before the introduction of catalyst-equipped cars and remains approximately the same with about 8% of vehicles on the road having catalytic converters. It is likely that some sulfate contribution can be expected from catalyst-equipped cars, however, other contributing factors may be important including the sulfur emissions from diesel vehicles and the possible conversion of ambient SO_2 to sulfate on filter surfaces.[17] Sulfuric acid samplers will soon be used in conjunction with particulate sulfate measurements to estimate the roadway H_2SO_4 contribution.

A similar monitoring study carried out by the New York State Department of Environmental Conservation is under way on a section of the heavily traveled Long Island Expressway. Unlike the LACS, the ROADS places primary emphasis on the micrometeorology associated with the highway and gives special attention to those parameters important in the determination of horizontal dispersion values, highway generated turbulence, and plume rise. In addition to measuring the distribution of sulfate, Pb, total particulate, and CO at an array of sampling points adjacent to the highway, the ROADS experiment includes a reevaluation of highway air pollution emissions factors from data derived in tracer gas experiments and a validation of the applicability of existing highway air pollution dispersion models.

The University of Wisconsin is developing a statistical model to describe the observed cross-freeway differences of automotive generated pollutants from the LACS. The Wisconsin model is an empirical time series rather than a diffusion model and is suited specifically for the LACS monitoring site and the meteorological conditions of Los Angeles. Basically, the model represents a statistical test of the effects of the catalyst on ambient pollutant concentrations with time. Concurrent efforts are under way at EPA with the HIWAY model.[18] Recent studies have shown that it estimates concentrations satisfactorily when winds are perpendicular to the roadway, but overestimates concentrations when winds are nearly parallel to the roadway.[19] It is thought that present techniques for specifying the horizontal dispersion parameter value result in overestimates because they do not account for low frequency meander in wind direction during the measurement period. The ROADS should provide the detailed meteorological data needed to test techniques for characterizing horizontal dispersion values and should result in improved HIWAY model accuracy.

Research Recommendations

The workshop participants agreed that long term monitoring programs are necessary to establish an empirical data base on H_2SO_4 roadway levels and that off-roadway monitoring should be complemented with in-roadway measurements. Suitable field measurement methods for H_2SO_4 together with field calibration, maintenance, and quality assurance procedures need to be incorporated in roadway monitoring projects to assure comparability of measurements. Procedures are needed for storing H_2SO_4 samples and other reactive samples for subsequent analysis when real time analyses are not possible. Improved methods for determining the number of catalyst-equipped cars in a total roadway population are also needed (presently used techniques in the California studies involve visual photographic discrimination based on license plate codes). Finally, workshop participants emphasized the need for further development of both determinative and statistical models to predict roadway emissions under a variety of meteorological, highway, and automotive population conditions.

Health and Ecological Effects

Current Status

Health effects research includes current experiments to determine toxicological and clinical effects resulting from the inhalation of H_2SO_4. Studies reported were generally performed at concentrations ranging between 20 $\mu g/m^3$ to 200 mg/m^3, utilizing both acute and chronic exposure regimens.

The *in vitro* studies on sulfate salts at Duke University have shown that exposure to $(NH_4)_2SO_4$ results in a release of histamine from both guinea pig lung fragments and perfused rat lung.[20] Ventilatory volume was reduced in the perfused lung after exposure to $(NH_4)_2SO_4$; this same response can be induced by histamine or blocked by an antihistamine. The rate of removal of sulfate was seen as a function of the associated cation. The relative rates of removal of various sulfate salts correspond well with the ranking of the toxicity of similar sulfate salts previously reported by Amdur.[21,22] The results are important in considering the health effects of H_2SO_4 because of the rapid reaction with ubiquitous ambient NH_3 to form $(NH_4)_2SO_4$.[6]

The effects of air pollutants on tracheal mucus production were investigated at the University of California at Davis. When rats were exposed for 14 days to H_2SO_4, there was an increase in mucus production as measured by secreted glycoprotein in cultured tracheal explants. Simultaneous exposure to O_3 further enhanced the secretion, but if the animal was allowed 7 days of recovery post-exposure, mucus secretion returned to control levels.

The metabolism of benzo(*a*)pyrene by perfused rabbit lungs following *in vivo* exposure to SO_2, crude air particles, and other compounds was investigated at the University of Cincinnati.[23] Significant differences in both the extent and pathway of metabolism of benzo(*a*)pyrene were found to result from exposure to SO_2, and other compounds. Expansion of the study to include H_2SO_4 is planned for the near future.

Animal studies were conducted on the effects of exposure to H_2SO_4 alone or in combination with other pollutants on susceptibility to viral or bacterial infection using the infectivity model.[24] At the Illinois Institute of Technology Research Institute, mice which had inhaled H_2SO_4 and carbon particles in varying concentrations were then challenged with aerosols of viable influenza virus of *Streptococcus pyogenes*. The ensuing pneumonia resulted in a significant enhancement of mortality and decrease in mean survival time in the pollutant exposed groups. Scanning electron microscope examinations of respiratory tract tissue of the exposed animals showed that all exposures produced a variety of morphological changes: heavy mucus coating, matted cilia, tears, and dying cells in the nasal cavity. These and

other alterations were more extensive at higher concentrations.

Acute infectivity studies were also performed at the EPA using O_3 and H_2SO_4, alone and sequentially, at concentrations sufficiently low that mice challenged with *S. pyogenes* exhibited no significant increased susceptibility with either pollutant alone. When the O_3 exposure preceded the H_2SO_4, there was a significant increase in mortality. It appears that this sequence may be quite important because no enhancement of mortality was observed when H_2SO_4 preceded O_3 exposure. Reduced ciliary activity was also observed with exposure to H_2SO_4, but not to O_3. Inflammatory response in deep lung however, was not produced by acid.

Stanford Research Institute compared effects of H_2SO_4 and O_3, alone and in combination. Exposures to high concentrations of H_2SO_4 alone produced no morphological injury to the respiratory tract. The O_3 induced increased turnover rate of alveolar epithelial cells appears to be enhanced by simultaneous exposure to H_2SO_4.

Other work at EPA focused on the effects of H_2SO_4 on the immune system and selected hematological parameters. The circulating lymphocytes of rabbits exposed 4 hours for two successive days exhibited an increase in tritiated thymidine incorporation of lymphocytes in both the presence and absence of a T cell mitogen. Studies on the humoral immune system indicated that there was no change in the number of antibody producing spleen cells in immunized mice exposed to H_2SO_4. Assays of the blood of rabbits exposed to H_2SO_4 for 2 hr showed a significant reduction in hematocrit, an increase in polymorphonuclear leucocytes and a decrease in lymphoctyes.

The effect of exposure to H_2SO_4 on the ability of donkeys to clear radiolabelled Fe_2O_3 particles, as well as other parameters such as pulmonary flow resistance, pulmonary compliance, and regional deposition is being studied at the New York University Institute of Environmental Medicine. Donkeys were intermittently exposed for 1 hr to submicrometer H_2SO_4 and also $(NH_4)_2SO_4$ aerosol. Clearance was significantly slowed by 1 hr exposures to H_2SO_4, whereas exposure to $(NH_4)_2SO_4$ showed no effect. Some animals developed a persistent slowing of clearance following repeated short term exposure, and normal clearance did not return for several months.

The effect of H_2SO_4 on respiratory carcinogenesis is being investigated at the New York University Medical Center. Tumor production will be studied in hamsters which received either (1) only benzo(*a*)pyrene by intubation, (2) benzo(*a*)pyrene and inhalation exposure to H_2SO_4, or (3) H_2SO_4 alone. Results to date are preliminary, but early data suggest that tumors appear earlier in animals which received benzo(*a*)pyrene plus H_2SO_4, than received benzo(*a*)pyrene alone. Major lung findings in animals receiving H_2SO_4 alone were edema, congestion, and thickening of lung tissue.

Studies of the effects of exposure to catalytically treated whole engine exhaust is under way at EPA. Animals of several species (rat, hamster, guinea pig) are being exposed both to irradiated and nonirradiated exhaust produced by an automobile engine equipped with an oxidation catalyst. To assure the presence of significant H_2SO_4 in the exhaust, the fuel burned is spiked with sulfur (as thiophene) and the engine is equipped with an air pump. Pulmonary function measurements (airway resistance and pulmonary compliance) of guinea pigs exposed chronically to both kinds of exhaust are in progress. Few differences were noted in effects of irradiated and nonirradiated exhaust, possibly because of the chemical similarity of the two exhaust streams.

The question of whether or not H_2SO_4 may be neutralized in the lung by NH_3 naturally secreted by the body was the subject of a study at the University of Washington. Preliminary measurements indicate that ammonia present in the body is sufficient to form $(NH_4)_2SO_4$ or $(NH_4)_2HSO_4$ from H_2SO_4 inhaled in concentrations from 13 to 520 $\mu g/m^3$. The site of the reaction or whether this reaction takes place during inspiration, exhalation, or in transition is unclear.

Studies of the effects on human health of exposure to H_2SO_4 at 100 $\mu g/m^3$ are planned by EPA. The first set of experiments scheduled to begin in the spring of 1977, will study effects on pulmonary function. Later studies are expected to include measurements of blood chemistry and immunological parameters. Initial studies will employ H_2SO_4 in the size range of 0.3 to 0.09 μm diameter representing an aged ambient sulfate aerosol. When technology becomes available, H_2SO_4 aerosol of about 0.05 μm diameter or smaller will be used to represent fresh particles emitted from catalyst-equipped vehicles.

Studies at the University of Minnesota on the effects of H_2SO_4 on vegetation involve exposure of several plant species to particles <0.5 μm diameter. Injury to the area exposed to H_2SO_4 was reported to be of the type associated with photochemical oxidants. The present experimental exposure resulted in marginal necrosis, which is different from the necrotic blotching previously reported[25] as the result of exposure to H_2SO_4 in droplet form. This may be due to an energy dependent translocation of sulfate ions.

Research Recommendations

The need for a broader program spanning a sufficient period of time to include long term, low level exposure studies at or near ambient levels of H_2SO_4 was identified. Epidemiological studies for identification of health risks associated with other pollutants should be expanded to include H_2SO_4 and related pollutants associated with vehicular emissions. Development and use of mathematical models can provide a better understanding of the physics of the deposition and distribution of inhaled pollutants in both animal and human respiratory systems.

Studies of the effects of exposure to H_2SO_4 on physiological response in humans are important. Both "ultrafine" (<0.1 μm) H_2SO_4 as identified in catalyst-equipped vehicle exhaust and the larger size (aged) particles (~0.3 μm) resulting from growth in ambient air should be compared in these studies.

Studies of the interactions of H_2SO_4 with other ubiquitous, toxic pollutants should be expanded to provide a more realistic assessment of the consequences of inhalation exposure to "real-world" mixtures of pollutants. It is recognized that such studies are difficult to design because of the judgment involved in choosing which of the myriad pollutants associated with vehicular emission should be studied. Interactions, however, play an important role in eliciting different responses from pollutants under simultaneous and sequential exposure modes.

Conclusions

Perhaps the most important thing we learned from the Hendersonville conference is the need for technical information exchange among researchers involved in broad-based multidisciplinary programs such as the *Catalyst Research Program*. Too often engineers and physical scientists have little appreciation or understanding of the problems faced by health effects investigators (and vice versa). At Hendersonville, we gained an appreciation for "the other guy's" problems. Health effects researchers in the program now understand that measuring H_2SO_4 in ambient air and generating an ultrafine H_2SO_4 aerosol for inhalation toxicity studies are difficult problems. Similarly, air monitoring scientists now have a better understanding of the problems inherent in the conduct of animal toxi-

cology and clinical studies on H_2SO_4 aerosols, and the difficulties encountered in analyzing and interpreting the results of biological experiments."

We also learned that the problems in assessing the environmental impact from automobile exhaust emissions are changing rapidly. For example, no problem with emission of platinum and palladium ablation products was seen with the production catalysts marketed. Now it appears that earlier estimates of H_2SO_4 emissions may have been higher than they actually are. Though average H_2SO_4 emissions of 36 mg/mi were measured for new California standard catalyst-equipped vehicles during the GM test study,[6] results reported here seem to indicate that emissions are probably much lower for in-use vehicles. Consequently, continuing monitoring and emissions characterization research is needed to discover and evaluate problems created by use of the catalytic converter to provide realistic information for designing toxicity studies.

Since exposures to combinations of H_2SO_4 and other pollutants such as ozone or carbon particles elicit response quite different from exposure to H_2SO_4 alone, pollutant interactions have emerged as an important area of the study. Care must be exercised in selecting appropriate compounds for study in order to simulate actual ambient mixtures.

Another need identified by conference participants is for the long term dedication of resources for specific well defined research problems. In rapidly changing programs such as the *Catalyst Research Program*, managers often place too much emphasis on short term projects which have a rapid pay off. The participants agreed that long term research commitments are essential, especially in determining chronic effects from H_2SO_4 and other sulfur compounds emitted from vehicles.

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Mention of commercial products does not imply endorsement by the Environmental Protection Agency.

Copies of the conference proceedings are available on written request from Ms. Frances (Vandy) Duffield, Catalyst Research Program, MD-83, U. S. Environmental Protection Agency, Research Triangle Park, NC 27711.

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